EUTECH INSTRUMENTS PTE LTD.
AMMONIA GAS-SENSING ELECTRODE
INSTRUCTION MANUAL

EUTECH
INSTRUMENTS
Technology Made Easy ...

TABLE OF CONTENTS

GENERAL INSTRUCTIONS

Introduction

Eutech Instruments Ammonia Gas-Sensing Electrode is used to quickly, simply, accurately, and economically measure dissolved ammonia in aqueous solutions. It can also be used to measure the ammonium ion after conversion to ammonia or organic nitrogen from Kjeldahl digestion of the sample. The measurement is not affected by sample color or turbidity and samples do not need to be distilled. Interference from anions, cations, and dissolved species, other than volatile amines, do not occur. With a flow-through cap, the electrode can be used in flow-through applications.

Required Equipment

1. A pH/mV meter or an ion meter, either line operated or portable.

2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode.

3. A magnetic stirrer.

4. Eutech Ammonia Gas-sensing Electrode, Code No. EC-NH3-01.

Required Solutions

1. Deionized or distilled water for solution preparation.

2. Eutech Ammonia Standard, 0.1M NH_4Cl, Code No. EC-SCS-AA1-BT. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 5.35 grams of reagent-grade NH_4Cl. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.

3. Eutech Ammonia Standard, 1,000 ppm NH_3 as N, Code No. EC-SCS-AA2-BT. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 3.82 grams of reagent-grade NH_4Cl. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.

4. Eutech Ammonia Standard, 100 ppm NH_3 as N, Code No. EC-SCS-AA3-BT. To prepare this solution from your own laboratory stock, half fill a one liter volumetric flask with distilled water and add 0.382 grams of reagent-grade NH_4Cl. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution.

5. Eutech Ionic Strength Adjuster (ISA) Solution, 10 M NaOH, Code No. EC-ISA-AA1-BT. To prepare this solution from your own laboratory stock, half fill a 1,000 ml beaker with distilled water, add 400 grams of reagent-grade NaOH (sodium hydroxide). Swirl the flask gently <u>under a hood</u> to dissolve the solid. Allow to cool and fill to the mark with distilled water. Stir the solution and store in a plastic bottle.

6.   Eutech Ionic Strength Adjuster (ISA) Solution, 5M NaOH/.05M Disodium EDTA/10% Methanol with Color Indicator, Code No. EC-ISA-AA2-BT. To prepare this solution from your own laboratory stock, half fill a 1,000 ml beaker with distilled water and add 200 grams of reagent-grade NaOH. Stir the solution to dissolve the pellets, add 18.61 grams of disodium EDTA, and stir the solution again until all solids have dissolved. Allow solution to cool. In a separate 150 ml beaker, add a tiny amount (10-20 mg) of thymolphthalein to 100 ml of methanol and stir to dissolve. Pour the methanol solution into the 1,000 ml beaker and stir to blend. The solution should turn a dark blue. Fill to the 1,000 ml mark with distilled water and stir to blend.

GENERAL PREPARATION

Electrode Preparation

This electrode is shipped dry. Before using, unscrew the large cap (See Figure 5), and remove the inner glass electrode from the outer body. Fill the outer body with 2 to 3 ml of internal filling solution. Place the inner glass electrode into the outer body, and screw on the large cap until finger tight. Place the assembled electrode in an electrode holder with a 20° angle from the vertical to avoid trapping air bubbles at the bottom of the electrode.

Checking Membrane

A small hole of any size on the membrane or breakage of the membrane causes failure of the electrode. It is recommended to check the membrane on every newly assembled electrode.

1.   Connect a newly assembled electrode to a pH/mV meter.

2.   Lower the electrode tip in distilled water.

3.   Record the reading after stirring the distilled water for about 15 minutes.

4.   Add proper ISA solution (see **Required Solutions**) to the distilled water. A drastic change in the reading in a negative direction indicates damage of the membrane.

Changing Membrane (see Figure 4)

1.   Unscrew the top cap from the outer body and remove the inner glass body from the epoxy outer body. Carefully place the glass body aside.

2.   Unscrew the bottom cap from the outer body. Remove the old membrane from around the threads and electrode tip opening.

3.   Using the tweezers provided, grab a new piece of white membrane material by the edge and remove from the separator paper. Then, with the hand not holding the tweezers, hold the electrode body up at the threads with thumb and forefinger. Place one edge of the membrane against the threads and hold in place with your thumb. Stretch new membrane lengthwise across the electrode opening so that it smoothly covers the opening. Place the other edge of the membrane against the threads and hold in place with your forefinger.

4. Place the bottom cap gently over the membrane onto the threads and screw the bottom cap on until finger-tight. Check that the membrane is free of wrinkles and holes or else repeat the above steps.

5. Using the syringe provided, fill the outer body with approximately 2 ml of inner filling solution. Place glass inner body into epoxy outer body containing the internal filling solution and screw on the upper cap until finger-tight.

Connecting the Electrode to the Meter

Connect the electrode to the meter according to meter manufacturer's instructions. No external reference electrode is required. To prevent air entrapment, mount the electrode at a 20° angle from the vertical.

Electrode Slope Check (with pH/mV meter)
(check electrodes each day)

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 1 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Remove air bubbles by redipping probe.

2. Using a pipet, add 1 ml of 0.1M or 1,000 ppm standard into the solution. When the reading has stabilized, record the mV value.

3. Using a pipet, add 10 ml of the same ammonia standard used above to the beaker. When the reading has stabilized, record the mV value.

4. Determine the difference between the two readings. The electrode is operating correctly if a difference of 56±3 mV is found, assuming the solution temperature is between 20° and 25^oC. See the **TROUBLESHOOTING** section if the potential change is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

Electrode Slope Check (with ion meter)
(check electrodes each day)

1. Prepare standard ammonia solutions whose concentrations vary by tenfold. Use either the 0.1M or 1,000 ppm ammonia standard. Use the serial dilution method for this preparation.

2. To a 150 ml beaker, add 100 ml of the lower value standard and 1 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the concentration mode.

3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.

4. Rinse the electrodes with distilled water and blot dry.

5.   To another 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.

6.   Adjust the meter to the concentration of the standard and fix the value in the memory.

7.   Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See **TROUBLESHOOTING** section if the slope is not within this range.

MEASUREMENT

Measuring Hints

Samples should be measured immediately after collection. Samples should be stored according to the directions given in **Sample Storage** if immediate measurement is not possible.

The ratio of a surface area to volume in the beaker should be minimized. Beakers containing the samples or the standard should be kept covered between measurements.

The ammonia ISA, 10M NaOH, should be added just before measurement. All samples and standards should be at the same temperature for precise measurement. A difference of $1^{o}C$ in temperature will result in approximately a 2% error. All samples must be aqueous.

Always rinse the electrode with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

Constant, but not violent, stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change solution temperature. To counteract this effect, place a piece of insulating material, such as gauze or styrofoam, between the beaker and the magnetic stirrer.

Always check to see that the membrane is free from air bubbles after immersion into standard or sample.

Sample Storage

Samples should be measured immediately after preparation or collection, if possible. Wait only long enough for temperature equilibration between the sample and the electrode. If stirring a 100 ml basic solution in a 150 ml beaker, the rate of ammonia loss at room temperature is about 50% in six hours. The loss of CO_2 increases with increasing temperature.

If the samples cannot be measured immediately, add 0.5 ml of 1M HCl to each liter of sample to make them slightly acidic (pH 6) and store in tightly capped vessels. Prior to measurement, add 10M NaOH to make the samples slightly basic.

Sample Requirements

Sodium hydroxide buffer must be added to standards and samples before measurement. When 10M NaOH is added, all standards and samples should be in the range of pH 11 to 14. In this range, all ammonium species are converted to ammonia. Adding the 10M NaOH adjusts the total level of

dissolved species below 1M. If the total level is greater than 1M, the sample should be diluted before measurement. For further explanation, see the section entitled **Effect of Dissolved Species**.

Units of Measurement

Measurement of ammonia can be expressed in units of moles/liter, ppm as nitrogen, ppm as ammonia, or other convenient concentration unit. Table 1 lists conversion units.

TABLE 1: Concentration Unit Conversion Factors

| moles/liter	ppm N	ppm NH$_3$
10^{-2}	140.0	170.0
10^{-3}	14.0	17.0
10^{-4}	1.4	1.7

MEASUREMENT PROCEDURE

Direct Measurement

Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with ISA for all ammonia solutions. The temperature of both sample solutions and standard solutions should be the same.

Direct Measurement of Ammonia (using a pH/mV meter)

1. By serial dilution, prepare three standard solutions from the 0.1M or 1,000 ppm stock standard. The resultant concentrations should be 10^{-2}M, 10^{-3}M, and 10^{-4}M or 1,000, 100 and 10 ppm ammonia standards. Add 1 ml of ISA per 100 ml of standard. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.

2. Place the most dilute solution (10^{-4}M or 10 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. After the reading has stabilized, record the mV value.

3. Place the mid-range solution (10^{-3}M or 100 ppm) on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrode with distilled water, blot dry, and immerse the electrode tip in the solution. When the reading has stabilized, record the mV value.

4. Place the most concentrated solution (10^{-2}M or 1,000 ppm) on the magnetic stirrer and begin stirring at a constant rate. After rinsing the electrode with distilled water, blot dry, and immerse the electrode tip in the solution. When the reading has stabilized, record the mV value.

5.   Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis). Extrapolate the calibration curve down to about $1.0 \times 10^{-5}M$. A typical calibration curve can be found in Figure 1.

Figure 1
Typical response of the ammonia electrode
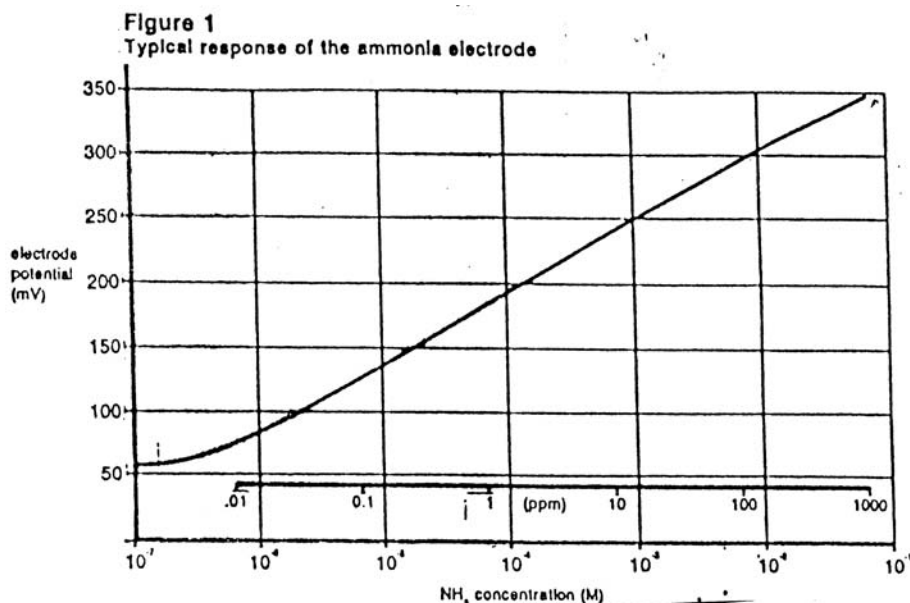
A calibration curve is constructed on semi-logarithmic paper when using the pH/mV meter in the millivolt mode. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.

6.   To a clean, dry 150 ml beaker, add 100 ml of sample and 1 ml of ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate. Rinse the electrodes with distilled water, blot dry, and lower the electrode tip into the solution. When the reading has stabilized, record mV reading. Using the calibration curve, determine sample concentration.

7.   The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of steps 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Ammonia (using an ion meter)

1.   By serial dilution of the 0.1M or 1,000 ppm ammonia standard, prepare two ammonia standards whose concentration is near the expected sample concentration. Add 1 ml of ISA to each 100 ml of standard.

2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.

3. Lower the electrode tip into the solution.

4. Adjust the meter to the concentration of the ammonia standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5. Rinse the electrode with distilled water and blot dry.

6. Place the most concentrated solution on the magnetic stirrer and begin stirring at a constant rate.

7. Lower the electrode tip into the solution. Adjust the meter to the concentration of the ammonia standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

8. For low level measurements, place the rinsed, dried electrodes into a solution containing 100 ml of distilled water and 1 ml of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.

9. Place 100 ml of the sample and 1 ml of ISA in a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring.

10. Lower the electrode tip in solution. When the reading has stabilized, read the concentration directly from the meter display.

11. The calibration should be checked every 2 hours. Assuming no change in ambient temperature, place the electrode tip in the first ammonia standard. After the reading has stabilized, compare it to the original reading in step 3 above. A reading differing by more than 0.5 units or a change in ambient temperature will necessitate the repetition of steps 2-8 above. The meter should be re-calibrated daily.

Low Level Ammonia Determination (using a pH/mV meter)

As the concentration of ammonia decreases, the rate of ammonia diffusion through the membrane is slow, the rate of equilibrium between the ammonium in the internal filling solution and ammonia is slow, and thus the response time increases. If the internal filling solution is diluted with ammonia-free distilled water (1:10), response at low levels can improve. Measurements can be speeded up by first placing the electrode tip in an ammonia-free pH 4 buffer, then into the sample. Always keep standards and samples covered. Work with large solution volumes to minimize surface-area-to-volume ratio, thereby avoiding ammonia absorption from air. Allow 5-10 minutes for a stable reading in the pH 4 buffer or a low-level solution.

Use the following low level ammonia measurement procedure in the non-linear portion of the calibration curve. (See Figure 1.) This procedure is used for ammonia samples containing less than 1.0×10^{-5} M ammonia.

1. Measure out 100 ml of a pH 4 buffer solution, add it to a 150 ml beaker, place the beaker on the magnetic stirrer, and begin stirring. Place the electrode tip in the solution for about 3 minutes.

2. By serial dilution, prepare a 10^{-2}M or 100 ppm ammonia standard by diluting the 0.1M or 1,000 ppm standard solution.

3. To a 2500 ml erlenmeyer flask, add 1,000 ml of distilled water and 10 ml of 10M NaOH. Place on magnetic stirrer and begin stirring. After rinsing the electrode, place the tip in this calibration solution. Assure that the meter is in the mV mode.

4. Using a 1 ml graduated pipet (A) and a 2 ml pipet (B), add increments of the 10^{-2}M or 100 ppm dilution to the calibration solution using the steps outlined in Table 2. Allow the reading to reach equilibrium and record the electrode potential after each step. Plot the concentration (log axis) vs. the electrode potential (linear axis) on semi-logarithmic paper to obtain the calibration curve.

5. After rinsing the electrode, immerse the electrode tip in pH 4 buffer for 3 minutes. Be sure to use the magnetic stirrer.

6. Place 1,000 ml of the sample into a 1,000 ml beaker, add 10 ml of 10M NaOH, place the beaker on the magnetic stirrer, and begin stirring. After rinsing the electrodes, immerse the tip in the solution. When the reading has stabilized, record the mV potential.

7. Determine concentration from the calibration curve. (Prepare a new low-level calibration curve on a daily basis using freshly prepared solutions).

TABLE 2: Additions of 10^{-2}M or 100 ppm Standard to 1,000 ml Distilled Water and 10 ml 10M NaOH

Step	Pipet	Added Volume(ml)	Concentration M	ppm
1	A	0.10	9.9×10^{-7}	0.01
2	A	0.10	2.0×10^{-6}	0.02
3	A	0.20	4.0×10^{-6}	0.04
4	A	0.20	5.9×10^{-6}	0.06
5	A	0.40	9.9×10^{-6}	0.10
6	B	2.00	3.0×10^{-5}	0.30
7	B	2.00	4.9×10^{-5}	0.49

Ammonia Measurements in Membrane Wetting Solutions

Since the membrane of the ammonia electrode is gas-permeable and hydrophobic, liquid water does not penetrate the membrane holes and does not wet it. A non-aqueous solution, or a solution containing a surfactant which wets the membrane, penetrates the membrane. Non-aqueous samples, such as latex paints or nylon, and those containing surfactants, such as sewage, cause measurement difficulties. The electrode must be suspended above the sample to measure ammonia in such samples.

Since water vapor reacts with ammonia in the gas phase, placing the ammonia electrode in a closed system containing water vapor will allow measurements of solutions above 10^{-3}M (14 ppm) to be taken.

Ammonia in samples containing non-aqueous solutions or surfactants can be measured by adjusting the sample pH to 11 to 13 with 10M NaOH. After measuring the sample, transfer it to an erlenmeyer flask large enough to contain approximately 2/3 volume of air after sample addition. Place a magnetic stir bar in the flask, fit the flask with a one-hole rubber stopper (opening large enough to insert the electrode snugly), and insert the electrode <u>until it is just above the level of liquid in the flask</u>. The closed flask now forms an air-tight closed system with the gas phase saturated with water vapor. The partial pressure of ammonia is in equilibrium with the solution.

For gas phase measurements, calibrate the electrode in a closed flask using standards. The response time for the ammonia electrode will be longer in the gas phase than if it were actually immersed in a surfactant-free, aqueous solution.

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the operating range of the electrode.

Interference

Volatile amines interfere with the operation of the ammonia electrode. Most gases, since they are converted to the ionic form in basic solutions, do not interfere with ammonia electrode measurement. The level of ions in solution can change the solubility of ammonia, though ionic species cannot cross the gas-permeable membrane and are not considered direct electrode interference. The level of ions in sample solution and standards do not interfere, given that they are equal. The same holds true for dissolved species. Low results can occur in direct measurements, due to the presence of some metallic ions and their complexation effect on ammonia.

Effect of Dissolved Species

One common substance that is a potential electrode interference is water vapor. The concentration of the internal filling solution under the membrane is changed when water, in the form of water vapor, moves across the electrode membrane. These changes will be seen as electrode drift. If the total level of dissolved species in solution, the osmotic strength, is below 1M and the sample and electrode temperatures are the same, water vapor transport is not a problem.

Samples of low osmotic strength are automatically adjusted to the correct level through addition of 10M NaOH. If samples have osmotic strengths greater than 1M, they should be diluted before measurement. However, this dilution should not reduce the ammonia level below 10^{-5}M. If dilution is not possible, for the reason mentioned, the sample can be measured by adjusting the osmotic strength of the electrode filling solution. The total level of dissolved species in the electrode filling solution may be adjusted by adding 0.425 grams of reagent-grade sodium nitrate ($NaNO_3$) to 10 ml of the electrode filling solution.

Complexation

Metal complexes are formed with ammonia and a number of metal ions. Complexes of mercury, copper, gold, silver, nickel, zinc, cobalt, and cadmium are removed in the form of hydroxide complexes or precipitates in basic solution. When ammonia concentration is below 10^{-3}M and hydroxide is present at the 10^{-1}M level, the only appreciable complex formed will be between mercury and ammonia. Since the total ammonia level of a sample will be measured if the mercury is preferentially bound to another species, addition of iodide is recommended for this purpose. Use of the recommended ISA (10M NaOH solution) inhibits the formation of metal complexes in the sample, since it contains a high concentration of hydroxide ions.

Temperature Influences

Table 4 gives the variation of theoretical response with temperature. The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10^{-3}M solution. Gases are expelled from a solution at a faster rate as the temperature increases.

TABLE 4: Temperature vs. Values for Electrode Slope

Temp.(°C)	"S"
0	54.20
5	55.20
10	56.18
15	57.17
20	58.16
25	59.16
30	60.15
35	61.14
40	62.13

Electrode Response

Plotting the electrode mV potential against the ammonia concentration on semi-logarithmic paper results in a straight line with a slope of about 56 mV per decade. (See Figure 1.)

For ammonia concentrations above 4×10^{-6}M (0.07 ppm NH_3 or 0.06 ppm N), the electrode exhibits good time response (95% of total mV reading in one minute or less). Response times are longer below this value and ammonia loss to air may become a source of error. Figure 2 indicates the time response of ammonia electrode to changes in the ammonia concentration.

Figure 2
Percent of ammonia and ammonium as a function of pH
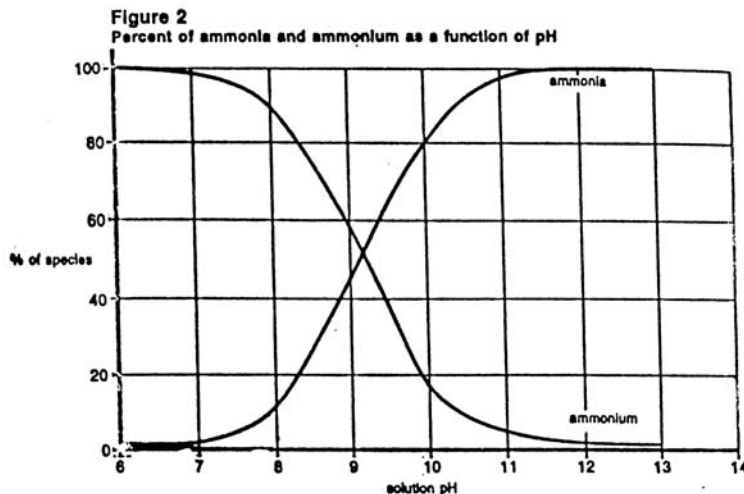
Limits of Detection

The upper limit of detection in pure ammonia solutions is 1M. Ammonia is rapidly lost to the air above a concentration of 1M. Dilution may be used if ammonia concentrations are above 1M. Also dilute samples between 1M and 10^{-1}M or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is around 1×10^{-6} M. Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of ammonia. Ammonia measurements below 10^{-5}M NH_3 should employ low level procedures.

pH Effects

The ammonia electrode can be used over the pH range 11 to 14. It is necessary to adjust the sample pH to above 11 using the recommended ISA to convert all ammonium species in solution to ammonia.

Electrode Life

The ammonia ion electrode will last six months in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and membrane replacement is required.

Electrode Storage

If erratic results are obtained from accidentally leaving the electrode in air, the space between the sensing element and the inside of the membrane may be dry. To remedy this situation and allow new filling solution to flow into the space, withdraw the glass electrode from the membrane by pulling the cable slightly.

For low level measurements, immerse the tip of the electrode in pH 4 buffer between measurements. For normal range measurements, keep the electrode tip immersed in a 0.001M or 10 ppm standard with added NaOH between measurements.

If storing the ammonia electrode overnight or over the weekend, immerse the tip in the 0.1M standard without added NaOH. Do not store overnight in pH 4 buffer.

For longer periods of time, completely disassemble the electrode, rinse the inner body, the outer body, and the cap with distilled water. After drying, reassemble the electrode without filling solution.

ELECTRODE THEORY

Electrode Operation

A gas-permeable membrane is used to separate the electrode's internal solution from the sample solution in the Eutech Ammonia Gas-Sensing Electrode. The sample diffuses dissolved ammonia through the membrane until the partial pressure of ammonia is the same on both sides of the membrane. The partial pressure of ammonia is proportional to the ammonia concentration.

The ammonia that diffuses through the membrane dissolves in the internal filling solution, reacting reversibly with water in the filling solution, to a small extent:

$$NH_3 + H_2O \Rightarrow NH_4^+ + OH^-$$
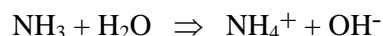
The equilibrium equation gives rise to the equilibrium constant in the following equation:

$$\text{constant} = \frac{[NH_4^+]\,[OH^-]}{[NH_3]}$$

The ammonium ion concentration can be considered fixed, since the internal filling solution contains ammonium chloride at a sufficiently high level. As a result:

$$[OH^-] = [NH_3] \text{ x constant}$$

The electrode sensing element's potential, with respect to the internal reference element, varies in a Nernstian manner with changes in the hydroxide level:

$$E = E_O - S \log [OH^-]$$

where S is the slope of the electrode.

Because the hydroxide concentration is proportional to the ammonia concentration, electrode response to ammonia is also Nernstian:

$$E = E_O^1 - S \log [NH_3]$$

E_O^1 represents the reference potential and is partly determined by the internal reference element which responds to the fixed level of chloride in the internal filling solution.

Ammonia Chemistry

As mentioned earlier, ammonia dissolves in water to form the ammonium ion. Ammonia also reacts with hydrogen (hydronium) ions to form ammonium ions:

$$NH_3 + H_3O^+ \Rightarrow NH_4^+ + H_2O$$
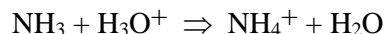
The relative amounts of the ammonium ion and of ammonia is determined by the solution's pH. Virtually, all the ammonia is converted to ammonium ion where hydrogen ion is readily available, as in acid solution. Half the ammonia will be in the form of ammonium ion at a pH of about 9.3. (See Figure 3).

Figure 3
Typical electrode response to step changes in ammonia concentration
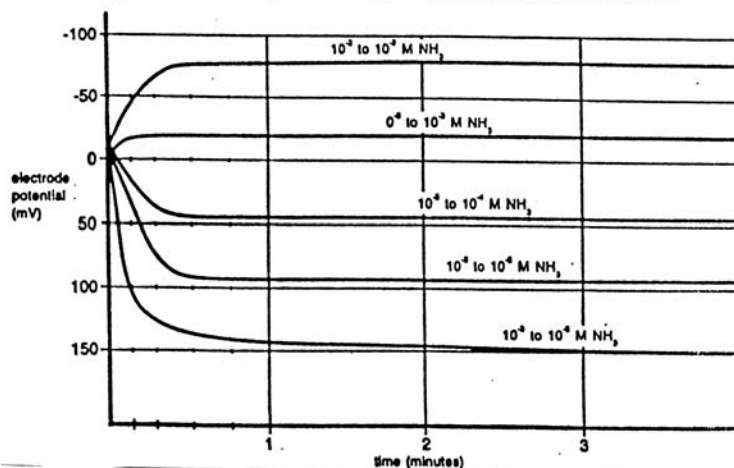
It is possible to calculate the ratio of ammonia to ammonium ion, theoretically, if the pH is known. A. Martell and R. Smith in <u>Critical Stability Constants</u>, Plenum Press, New York, 1974, state:

$$\frac{[NH_4^+]}{[H_3O^+]} = \frac{[NH_4^+]}{[NH_3]} \quad \frac{}{10^{-pH}[NH_3]} \quad K \sim 10^{-9.3}$$

at $25^{\circ}C$, $X = 0.1$ where $pH \sim 9.3$

The ratio of ammonium to ammonia is given by:

$$\frac{[NH_4^+]}{[NH_3]} = K^{-pH} = 10^{\,9.3\text{-}pH}$$

Both temperature and ionic strength will cause the exact value of K to vary. If, for example, while the pH at $25^{\circ}C$ and $X = 0.1$ is 9.3, an increase in ionic strength to $X = 1.0$ yields a pH of 9.4, at $25^{\circ}C$.

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glassware the electrodes, the standard and reagents, the sample, and the technique.

Meter

The meter is the easiest component to eliminate as a possible cause of error. Most meters are provided with an instrument check-out procedure in the instruction manual and a shorting strap for convenience in troubleshooting. Consult the manual for complete instructions and verify that the instrument operates as indicated and is stable in all steps.

Glassware

Clean glassware is essential for good measurement. Be sure to wash the glassware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

Electrodes

The electrodes may be checked by using the procedure found in the section entitled **Electrode Slope Check**.

1. Be sure to use either distilled or deionized water when following the procedures given in **Electrode Slope Check**.

2. If electrode fails to response as expected, see the sections entitled **Electrode Assembly** and **Checking Membrane.** Repeat electrode slope check.

3. If the electrode still does not perform as described, determine whether the ammonia electrode inner body is working properly as directed in **Checking the Electrode Inner Body.**

4. If the stability and the slope check out properly, but measurement problems persist, the standards may be of poor quality, the sample may contain interference or complexing agents, or the technique may be in error. (See **Standard, Sample** and **Technique** sections below.)

5. Before replacing a "faulty" electrode, review the instruction manual and be sure to:
   - Clean and rinse the electrode thoroughly.
   - Prepare the electrode properly.
   - Use proper filling solution, buffer, and standards.
   - Measure correctly and accurately.
   - Review **TROUBLESHOOTING HINTS**.

Standards

The quality of results depends greatly upon the quality of the standards. ALWAYS prepare fresh standards when problems arise. It could save hours of frustrating troubleshooting! Error may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is by serial dilution. This means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

Sample

If the electrode works properly in standards but not in sample, look for possible interference, complexing agents, or substances which could affect response or physically damage the sensing electrode or the reference electrode. If possible, determine the composition of the samples and check for problems. See **Sample Requirements** and **Interference**.

Technique

Be sure that the electrode's limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample. Refer to the instruction manual again. Reread the sections **GENERAL PREPARATION** and **ELECTRODE CHARACTERISTICS**.

If trouble still persists, call Eutech Instruments Pte Ltd. at (65) 6778-6876 and ask for the Customer Services Department.

TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	perform meter checkout procedure (see meter instruction manual)
	defective inner body	refer to **Checking the Electrode Inner Body**
	electrode not plugged in properly	unplug electrode and reset
	internal filling solution not added	fill outer body of electrode with proper amount of internal filling solution
	air bubble on membrane	remove bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Reading (readings continuously or randomly changing.)	insufficient internal filling solution	fill outer body of electrode with proper amount of internal filling solution
	defective meter	perform meter checkout procedure (see meter instruction manual)
	bottom cap loose	ensure that bottom cap is screwed on tight enough to close gap between bottom cap and body
	defective inner body	refer to **Checking the Electrode Inner Body**
	air bubbles on membrane	remove bubbles by redipping electrode
	meter or stirrer improperly grounded	check meter and stirrer for grounding
Drift (reading slowly changing in one	internal filling solution leakage	ensure that membrane is installed properly
	incorrect internal filling solution	refill outer body of electrode using filling solution shipped with electrode
	total sample level	dilute sample of dissolved species above 1M
	electrode in sample too long; NH_3 loss	reduce surface area to volume ratio, slow down rate of stirring, avoid

		high temperatures
	membrane failure (wet, perforation, discoloration)	replace membrane
	samples and standards standards not at constant temperature	allow samples and standards to come to room temperature before use
	heat generated by magnetic stirrer	place insulating material between stirrer and beaker
	defective inner body	refer to **Checking the Electrode Inner Body**
	electrode exposed to air for extended period	hold electrode by outer body and pull on electrode cable. Internal filling solution will flow under membrane and restore electrode response
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	buffer not used	use recommended buffer
	standard used as buffer	use buffer
	electrode exposed to air for extended period	hold electrode by outer body and pull on electrode cable. internal filling solution will flow under membrane and restore electrode response
	membrane failure (wet, perforation, discoloration)	replace membrane
	defective inner body	refer to **Checking the Electrode Inner Body**
"Incorrect Answer" (but calibration curve is good)	incorrect scaling of semi-log paper	plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	incorrect sign	be sure to note sign of millivolt

	value correctly
incorrect standards	prepare fresh standards
wrong units used	apply correct conversion factor: $10^{-3}M = 17$ ppm as $NH_3 = 14$ ppm as N
buffer added to standards and not samples	add same proportions of buffer to standards and samples
sample carryover	rinse electrodes thoroughly between samples

Checking the Electrode Inner Body

If the electrode slope is found to be low during operation, the following solutions will be necessary to check the inner body:

- pH 4 Buffer (0.1M NaCl added)
Add 2.9 grams of reagent-grade NaCl to 500 ml of pH 4 buffer. Dissolve the solid. The solution may be stored for repeated use.

- pH 7 Buffer (0.1M NaCl added)
Add 2.9 grams of reagent-grade NaCl to 500 ml of pH 7 buffer. Dissolve the solid. The solution may be stored for repeated use.

Disassemble the ammonia electrode. If the electrode is dry, soak the glass tip of the inner body in Eutech Ammonia Electrode Filling Solution (Code No. EC-RE-032) for at least two hours.

Rinse the electrode thoroughly with distilled water. Put 100 ml of pH 7 buffer (0.1M NaCl added) in a 150 ml beaker. Place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the inner body in the solution so that the reference element is covered. Make sure that the meter is in the mV mode. Record the meter reading when stable.

Rinse the inner body thoroughly in distilled water. Put 100 ml of pH 4 buffer (0.1M NaCl added) in a 150 ml beaker, place the beaker on the magnetic stirrer, and begin stirring. Immerse the tip of the inner body in the solution so that the reference element is covered. Observe the change in the meter reading carefully. In less than 30 seconds after immersion, the reading should change 100 mV. The meter reading should stabilize in 3 - 4 minutes, with a difference greater than 150 mV if the inner body sensing elements are operating properly.

SPECIFICATIONS

Concentration Range: 5×10^{-7}M to 1 M NH_3
(0.01 to 17,000 ppm NH_3)
(0.01 to 14,000 ppm as N)

pH Range: above 11

Temperature Range: 0° to 50^oC

Inner Body Resistance: ~1,000 Mohm

Reproducibility: $\pm$ 2%

Size: 110 mm length; 12 mm diameter; 1 m cable length

Storage: Store electrodes in 0.1M NH_4Cl

ORDERING INFORMATION

CODE NO.	DESCRIPTION
EC-NH3-01	Ammonia Gas Sensing Electrode
EC-MIS-AM	Ammonia Membrane Kit, bag of 20 membranes and spare o-ring
EC-SCS-AA1-BT	Ammonia Standard, 0.1M NH_4Cl
EC-SCS-AA2-BT	Nitrogen Standard, 1,000 ppm NH_3 as N
EC-SCS-AA3-BT	Nitrogen Standard, 100 ppm NH_3 as N
EC-ISA-AA1-BT	Ammonia Ionic Strength Adjuster (ISA) Solution, 10 M NaOH
EC-ISA-AA2-BT	Ammonia Ionic Strength Adjuster (ISA) Solution, 5M NaOH/.05M Disodium EDTA/10% Methanol with Color Indicator.